(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 432 861 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **90250311.9**

(22) Date of filing: **14.12.90**

(51) Int. Cl.5: **C07C 69/618**, C07C 69/63, C07C 69/65, C07C 69/734, C07C 69/76, C07C 69/92, C07C 233/09, A01N 37/00, C07C 67/00

(30) Priority: **15.12.89 DE 3941966**

(43) Date of publication of application: **19.06.91 Bulletin 91/25**

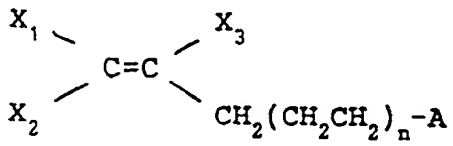
(84) Designated Contracting States: **AT BE CH DE DK ES FR GB GR IT LI LU NL SE**

(71) Applicant: **SCHERING AKTIENGESELLSCHAFT**
Müllerstrasse 170/178 Postfach 65 03 11
W-1000 Berlin 65(DE)

(72) Inventor: **Köhn, Arnim, Dr.**
Alt-Wittenau 63c
W-1000 Berlin 26(DE)
Inventor: **Hömberger, Günter, Dr.**
Waldmannstrasse 21
W-1000 Berlin 46(DE)
Inventor: **Joppien, Hartmut, Dr.**
Juttastrasse 18
W-1000 Berlin 37(DE)
Inventor: **Von Keyserlingk, Harald, Dr.**
Markgrafenstrasse 38
W-1000 Berlin 28(DE)
Inventor: **Sanft, Ulrich, Dr.**
Speerweg 12
W-1000 Berlin 28(DE)
Inventor: **Franke, Heinrich, Dr.**
Fabeckstr. 38
W-1000 Berlin 33(DE)
Inventor: **Wegner, Peter, Dr.**
Münchener Str. 3
W-1000 Berlin 28(DE)

(54) **Halogenated olefines, process for the preparation thereof and their use as pesticides.**

(57) There are described new halogenated olefines of general formula I



(I)

in which X_1, X_2, X_3, n and A have the meanings given in the description as well as processes for their preparation. The compounds can be used as pesticides especially against insects and acarids.

EP 0 432 861 A1

alkenyl, haloaryl-C_{1-6}-alkyl, C_{1-4}-alkylaryl-C_{1-4}-alkyl, haloaryl-C_{2-6}-alkenyl, halo-C_{1-4}-alkylaryl-C_{1-6}-alkyl, C_{1-3}-alkoxyaryl-C_{1-6}-alkyl, aryloxybenzyl, halophenyl-(cyclopropyl)-C_{1-3}-alkyl, halophenoxy-C_{1-6}-alkyl, naphthyl-C_{1-6}-alkyl,
aryl, optionally substituted, one or more times, by C_{1-20}-alkyl, halo-C_{1-6}-alkyl, C_{1-16}-alkoxy, halo-C_{1-6}-alkoxy, phenyl-C_{1-6}-alkyl, phenyl-C_{1-6}-alkoxy, C_{3-10}-cycloalkoxy, halo-C_{3-10}-cycloalkoxy, C_{3-6}-cycloalkylalkoxy, halo-C_{3-5}-cycloalkylalkoxy, C_{2-6}-alkenyloxy, halo-C_{2-6}-alkenyloxy, C_{2-6}-alkynyloxy, alkylsulphonyloxy, haloalkylsulphonyloxy, phenyl, halo, amino, cyano, hydroxy, nitro, C_{1-6}-alkoxycarbonyl, C_{1-6}-alkoxycabonylmethyl, halo-C_{1-6}-alkoxycarbonyl, C_{1-2}-alkyldioxy, C_{1-5}-alkylthio, halo-C_{3-6}-cycloalkylalkylcarbonyloxy, C_{1-6}-alkylamino or di-C_{1-6}-alkylamino,
heteroaryl, optionally substituted by halogen, C_{1-3}-alkyl or halo-C_{1-3}-alkyl, or

R^2 and R^3 together with the N-atom to which they are attached form a saturated or unsaturated heterocyclic ring,

R^4 is hydrogen or $-CH(R^5)COOR^8$,

R^5 is hydrogen, C_{1-20}-alkyl, C_{2-20}-alkenyl, C_{2-20}-alkynyl, optionally substituted benzyl, aryl or heteroaryl, as well as C_{1-20}-alkyl, C_{2-20}-alkenyl and C_{2-20}-alkynyl, substituted by $-Y-R^7$, $-COOR^7$, $-NR^7R^8$, $-OCONH_2$, $-NH-C(=NH)-NH_2$,

R^7 and R^8 are hydrogen or C_{1-6}-alkyl,

Y is oxygen or sulphur, and

R^6 is hydrogen, an alkali metal atom, a corresponding equivalent of a divalent atom or an ammonium or phosphonium cation with 0-4 alkyl, aryl or aralkyl groups, C_{1-20}-alkyl, C_{2-20}-alkenyl, C_{2-20}-alkynyl, halo-C_{3-6}-cycloalkyl-C_{1-6}-alkyl, C_{3-6}-cycloalkyl, C_{1-3}-alkyl-C_{3-6}-cycloalkyl, decalinyl, difluorocyclopropylethylcarbonyloxy-C_{1-10}-alkyl, difluorocyclopropylcarbonyloxydecalinyl, difluorocyclopropylethylcarbonyloxy-C_{1-3}-alkoxy-C_{1-3}-alkyl, phenyl-C_{1-6}-alkyl, phenyl-C_{2-6}-alkenyl, halobenzyl, C_{1-4}-alkylbenzyl, C_{1-3}-alkoxyphenyl-C_{1-6}-alkyl, phenoxybenzyl, α-cyanophenoxybenzyl, α-C_{1-3}-alkylphenoxybenzyl, halophenoxy-C_{1-6}-alkyl, naphthyl-C_{1-6}-alkyl,
aryl, optionally substituted, one or more times, by C_{1-20}-alkyl, halo-C_{1-6}-alkyl, C_{1-16}-alkoxy, halo-C_{1-6}-alkoxy, phenyl-C_{1-6}-alkyl, phenyl-C_{1-6}-alkoxy, C_{3-10}-cycloalkoxy, halo-C_{3-10}-cycloalkoxy, C_{3-6}-cycloalkylalkoxy, halo-C_{3-6}-cycloalkylalkoxy, C_{2-6}-alkenyloxy, halo-C_{2-6}-alkenyloxy, C_{2-6}-alkynyloxy, halo-C_{2-6}-alkynyloxy, alkylsulphonyloxy, alkylphenylsulphonyloxy, haloalkylsulphonyloxy, phenyl, halo, amino, cyano, hydroxy, nitro, aryloxy, heteroaryloxy, haloaryloxy, arylamino, haloarylamino, C_{1-6}-alkoxycarbonyl, C_{1-6}-alkoxycarbonylmethyl, halo-C_{1-6}-alkoxycarbonyl, C_{1-2}-alkyldioxy, C_{1-6}-alkylthio, halo-C_{3-6}-cycloalkylalkylamino, halo-C_{3-6}-cycloalkylalkylcarbonyloxy, C_{1-6}-alkylamino or di-C_{1-6}-alkylamino,
heteroaryl, optionally substituted by halogen, C_{1-3}-alkyl or halo-C_{1-3}-alkyl,

and R^4 and R^1 together with the N-atom to which they are attached can form a saturated or unsaturated heterocyclic ring,

with the proviso that when X_1 and X_3 are both fluoro or when X_1 is chloro and X_3 is hydrogen, n is not O, and when X_1 is fluoro and X_3 is trifluoromethyl and n is O, R^1 is not ethyl, show better insecticidal and acaricidal activity in comparison to the known compounds of related structure.

Preferred compounds are those where X_1 is fluoro.

The term "alkyl" includes straight and branched carbon chains.

The term "alkenyl" includes straight and branched carbon chains that can contain one or more double bonds.

The term "alkynyl" includes straight and branched carbon chains that can contain one or more triple bonds.

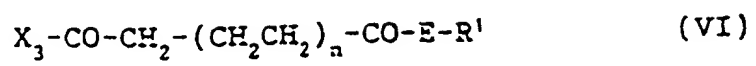
The term "aryl" means one to three ringed aromatic groups, such as phenyl, naphthyl or phenanthryl.

The term "heteroaryl" means a 5- or 6-membered ring that contains one or more nitrogen, oxygen or sulphur atoms that can be saturated or partially saturated and can optionally carry a fused benzo ring, eg pyridine, thiazole or chromene.

When R^2 and R^3 as well as R^1 and R^4 together with the atom to which they are attached form a saturated or unsaturated heterocyclic ring, these may be for example morpholino, piperidino, pyrrolo, imidazolo, triazolo or pyrrolidino.

The compounds of general formula I can exist as mixtures of optical isomers. In such cases the invention also includes the individual isomers of the compounds of formula I as well as their mixtures.

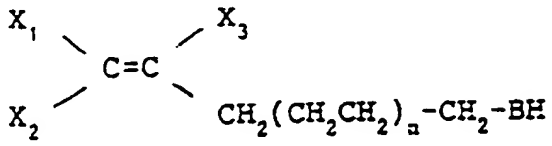
intermediate compound of formula VI



(VI)

wherein X_3, n, E and R^1 have the meanings given in general formula I and, in the presence of an inert solvent, this is reacted with a halomethane or an alkaline metal salt of a trihaloacetic acid and a trisubstituted phosphine, or

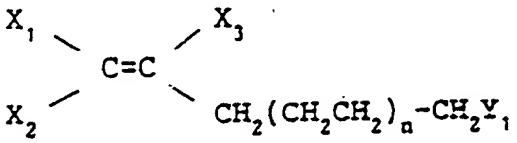
d) an alcohol of general formula III



(III)

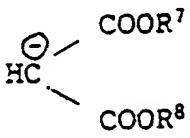
in which X_1, X_2, X_3, n and B have the meanings given in general formula I, is reacted with an oxidising agent, optionally using a solvent, to give an acid of general formula II which is then further treated according to process variant b), or

e) a halide of general formula VII



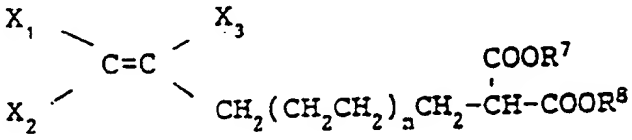
(VII)

in which X_1, X_2, X_3 and n have the meanings given in general formula I and Y_1 is chlorine, bromine or iodine, is reacted, optionally in the presence of a solvent, with an anion or a diester of malonic acid of general formula VIII



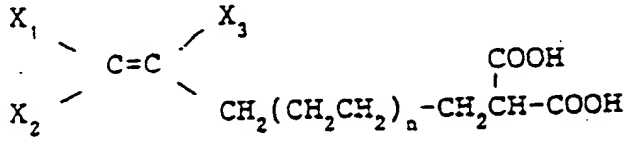
(VIII)

wherein R^7 and R^8, independently of each other are C_{1-10}-alkyl, aryl or benzyl, to give an intermediate compound of general formula IX



(IX)

wherein X_1, X_2, X_3 and n have the meanings given in general formula I and R^7 and R^8 have the meanings given above and this is then converted by acid or alkaline hydrolysis to give an intermediate compound of general formula X



(IX)

in which X_1, X_2, X_3 and n have the meaning given in general formula I and this is monodecarboxylated by heating or by using a catalyst, optionally in the presence of the solvent, and then further reacted

in which B, D and R^1 have the meaning given in general formula I, optionally using a solvent as well as a catalyst, or
i) an alcohol of general formula III is reacted with an acid halide of general formula XIV

$$R^1\text{-}CO\text{-}Y_1 \qquad \text{(XIV)}$$

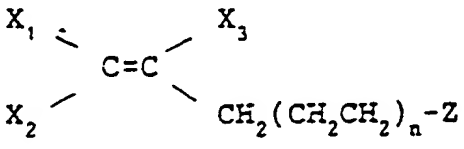
in which Y_1 is chlorine or bromine and R^1 has the meaning given in general formula I, optionally using a solvent as well as an acid acceptor, or
j) an alcohol of general formula XV

$$X_3\text{-}CO\text{-}CH_2\text{-}(CH_2CH_2)_n\text{-}CH_2OH \qquad \text{(XV)}$$

wherein n and X_3 have the meanings given in general formula I, is reacted with an acid of general formula XIII, optionally using a solvent as well as a catalyst, to give an intermediate compound of general formula XVI

$$X_3\text{-}CO\text{-}CH_2\text{-}(CH_2CH_2)_n\text{-}CH_2\text{-}B\text{-}\underset{\underset{D}{\|}}{C}\text{-}R^1 \qquad \text{(XVI)}$$

in which X_3, n, B, D and R^1 have the meanings given in general formula I and then, in the presence of an inert solvent, this is reacted with a halogenated C_1-unit according to process variant c), or
k) an alcohol of general formula XV is reacted with an acid halide of general formula XIV, optionally using a solvent as well as an acid acceptor, to give an intermediate compound of formula XVI and this is then reacted with a halogenated C_1-unit according to process variant c), or
l) a halide or general formula XVII

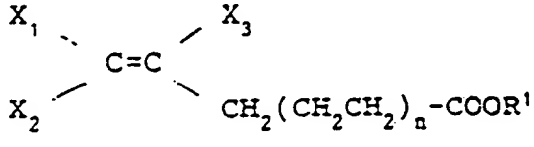


(XVII)

in which X_1, X_2, X_3 and n have the meanings given in general formula I and Z is chlorine, bromine or iodine, is reacted with a carboxylate salt of general formula XVIII

$$R^1COOM \qquad \text{(XVIII)}$$

in which R^1 has the meaning given in general formula I and M is a monovalent metal or the corresponding equivalent of a multivalent metal, optionally using a solvent as well as a catalyst, or
m) an acid or ester of general formula XIX



(XIX)

in which X_1, X_2, X_3, n and R^1 have the meanings given in general formula I is reacted with a reducing agent, optionally using a solvent, to give an alcohol of general formula III which is then treated according to process variant d) or e).

The reactions can be carried out over a wide temperature range. Generally they are carried out at a temperature between -20° and 200° C.

The reactions are preferably carried out at atmospheric pressure, although higher or lower pressures

undecimpunctata); Orthoptera, such as Blattella germanica; ticks, such as Boophilus microplus and lice, such as Damalinia bovis and Linognathus vituli, as well as mites such as Tetranychus urticae and Panonychus ulmi.

The compounds according to the invention can be used at a concentration of 0.0005 to 5%, preferably from 0.001 to 1%, calculated as gram active material per 100 ml of the composition.

The compounds of the invention can be used either alone or in mixture with each other or another insecticide. Optionally other plant protection or pesticidal compositions, such as for example insecticides, acaricides or fungicides can be added depending on the desired result.

An improvement in the intensity and speed of action can be obtained, for example, by addition of suitable adjuvants, such as organic solvents, wetting agents and oils. Such additives may allow a decrease in the dose.

Suitable mixture partners may also include phospholipids, e.g. such as from the group phosphatidylcholine, hydrated phosphatidylcholine, phosphatidylethanolamine, N-acyl-phosphatidylethanolamine, phosphatidylinositol, phosphatidylserine, lysolecithin or phosphatidylglycerol.

The designated active ingredients or their mixtures can suitably be used, for example, as powders, dusts, granules, solutions, emulsions or suspensions, with the addition of liquid and/or solid carriers and/or diluents and, optionally, binding, wetting, emulsifying and/or dispersing adjuvants.

Suitable liquid carriers are, for example aliphatic and aromatic hydrocarbons such as benzene, toluene, xylene, cyclohexanone, isophorone, dimethyl sulphoxide, dimethylformamide, other mineral-oil fractions and plant oils.

Suitable solid carriers include mineral earths, e.g. tonsil, silica gel, talcum, kaolin, attapulgite, limestone, silicic acid and plant products, e.g. flours.

As surface-active agents there can be used for example calcium lignosulphonate, polyoxyethylenealkylphenyl ether, naphthalenesulphonic acids and their salts, phenolsulphonic acids and their salts, formaldehyde condensates, fatty alcohol sulphates, as well as substituted benzenesulphonic acids and their salts.

Formulations can be prepared, for example, from the following ingredients.

Benzyl 5-oxohexanoate

43.27 g (0.628 mol) Anhydrous potassium carbonate and a spatula full of sodium iodide was added to a solution of 50 g (0.385 mol) 5-oxohexanoic acid and 45.87 ml (0.385 mol) benzyl bromide in 380 dimethylformamide. After stirring for one hour at 100 °C, the solvent was evaporated in a rotary evaporator. The residue was diluted with 250 ml water and extracted with ether. The ether phase was washed until it was neutral and concentrated.

Yield 81.28 g (95.9%)

R_f = 0.50 (hexane/ethyl acetate = 1/1)

The product was used without further purification.

Example 2

Process variant f)

3-Phenoxybenzyl 6,6-difluoro-5-methyl-5-hexenoate

A solution of 1.75 g 6,6-difluoro-5-methyl-5-hexanenitrile (see Example 23) and 2.42 g 3-phenoxybenzyl alcohol in 15 ml absolute ether was saturated at 5 °C with HCl and stirred at 3 °C for 6 hours. After standing for 14 hours at room temperature, the mixture was treated with 50 ml water and brought to pH 4.5 with 10% aqueous sodium hydroxide. The ether was then distilled over 1 hour under reflux. 100 ml hexane was then starred in and the separated organic phase washed twice with 100 ml water. After drying over calcium chloride and evaporation of the solvent in vacuo, the remaining residue was purified by column chromotography (silica gel; ethyl acetate/hexane = 1/20).

Yield: 1.96 g (47%)

R_f = 0.73 (ethyl acetate $n^{22.4}_D$ = 1.52332

Example 3

6,6-Difluoro-5-methyl-5-hexanoic acid

1.27 g of the product of Example 1 was added to a solution of 0.36 g potassium hydroxide and 2 ml methanol. After stirring for two hours at room temperature, the reaction mixture was poured into water and treated with 5 ml 1N aqueous sodium hydroxide. The mixture was then washed 4 times with ethyl acetate. The aqueous phase was acidified with dilute hydrochloric acid and extracted with ethyl acetate. The organic phase was washed with saturated aqueous sodium chloride, dried over sodium sulphate and concentrated.

Yield: 0.70 g (85.3%)

R_f = 0.47 (Hexane/ethyl acetate = 1/1)

n_D^{20} = 1.4057

Example 4

6,6-Difluoro-5-methyl-5-hexenoyl chloride

4.09 ml (56.29 mmol) Thionyl chloride was added dropwise to 3.50 g (21.32 mmol) of the product of Example 3 at room temperature. A drop of dimethylformamide was then added and the mixture heated for 6 hours under reflux. It was then distilled under reduced pressure.

Yield: 2.64 g (68%)

bp : 56-59 °C/26 mbar

Example 5

Process variant b)

1-Pyrrolidinylcarbonylmethyl 6,6-difluoro-5-methyl-5-hexenoate

A solution of 0.82 g (5 mmol) of the product of Example 3 and 0.6 g (5 mmol) N-(bromoacetyl)-pyrrolidine in 5 ml dimethylformamide was treated at room temperature with 0.1 g sodium iodide and 0.7 ml

6,6-Difluoro-5-hexenoic acid

A solution of 6 g (106.9 mmol) KOH flakes and 19.0 g (120.6 mmol) or the product of Example 8 in 50 ml methanol was stirred at room temperature overnight. The mixture was then concentrated on a rotary evaporator. The residue was dissolved in 40 ml water and washed twice with ether. The aqueous phase was acidified with 1N hydrochloric acid and extracted 4 times with ether. The ether phase was washed with water, dried over sodium sulphate, filtered and concentrated in a rotary evaporator.

Yield: 15.3 g (84.5%)
R_f = 0.45 (hexane/ethyl acetate = 1/1)
n_D^{20} = 1.4048

Example 10

6,6-Difluoro-5-hexenoyl chloride

10.23 ml (140.68 mmol) Thionyl chloride was added dropwise to 8.0 g (52.29 mmol) of the product of Example 9 at room temperature. A drop of dimethylformamide was added and the mixture heated under reflux for 6 hours. It was then distilled under reduced pressure.

Yield 6.6 g (73.5%)
bp = 52-54° C/36 mbar

Example 11

Process variant b)

2-Naphthylmethyl 6,6-difluoro-5-hexenoate

A solution of 0.83 ml (5 mmol) diethyl azodicarboxylate was added, dropwise, slowly, at room temperature to a solution of 0.75 g (5 mmol) of the product of Example 9, 0.79 g (5 mmol) 2-Naphthylmethanol and 1.34 g (5.1 mmol) triphenylphosphine in 15 ml tetrahydrofuran. After stirring for 6 hours at room temperature, the reaction mixture was concentrated in a rotary evaporator. The crude product was purified by column chromatography (silica gel; hexane: ethyl acetate = 8.2).

Yield: 0.89 g (61%)
R_f = 0.25 (Hexane: toluene - 1:1)
n_D^{20} = 1.5408

Example 12

Process variant a)

Methyl N-(6,6-difluoro-5-hexen-1-oyl)-L-phenylalaninate

0.84 g (5 mmol) 6,6-Difluorohex-5-enoyl chloride was added, dropwise, slowly, to a solution of 1.08 g (5 mmol) methyl L-phenylalaninate hydrochloride and 0.1 g 4-dimethylaminopyridine in 20 ml pyridine under ice-bath cooling. After stirring for 16 hours at room temperature, the reaction mixture was poured into 20 ml ice-water and extracted with ethyl acetate. The organic phase was washed once with 20 ml water, dried over sodium sulphate, filtered and concentrated on a rotary evaporator. The residue was purified by column chromatography (silica gel; hexane: ethyl acetate = 1:1).

Yield: 1.40 g (94%)
R_f = 0.21 (Hexane: ethyl acetate = 1:1)
n_D^{20} = 1.4965

Example 13

Process variant j)

1-Benzoyloxy-6,6-difluoro-5-hexene

R_f = 0.75 (ethyl acetate)
n_D^{20} = 1.4920

Example 16

Process variant e)

5,6,6-Trifluoro-5-hexanoic acid

A solution of 6.70 g (28.34 mmol) 2-(3,4,4-trifluoro-3-butenyl)malonic acid in 40 ml xylene was heated for 8 hours under reflux. After cooling the mixture was diluted with 100 ml ether and extracted 3 times with 50 ml 1N aqueous sodium hydroxide. The aqueous phase was washed with 50 ml ether and then acidified with dilute hydrochloric acid. It was then extracted 4 times with 50 ml ether each time. The combined ether extract was washed with aqueous sodium chloride, dried over sodium sulphate, filtered and concentrated. The residue was used without further purification.

Yield: 3.36 g (70.10%
R_f = 0.55 (ethyl acetate)

Preparation of the Starting Material

Dibenzyl 2-(3,4,4-trifluoro-3-butenyl)malonate

10.9 g (100.8 mmol) Benzyl alcohol was added slowly dropwise to a suspension of 3.18 g (105.8 mmol) 80% sodium hydride in white oil in 100 ml THF. The mixture was then heated under reflux for 1 hour. 28.66 g (100.8 mmol) Benzyl malonate was added then added dropwise at 50° C. After stirring for 1 hour 20 g (105.8 mmol) 4-bromo-1,1,2-trifluoro-1-butene was added dropwise. The reaction mixture was stirred overnight at room temperature and then heated at reflux for a further 4 hours. After cooling, the reaction mixture was poured into 100 ml ice-water and extracted with ethyl acetate. The ethyl acetate phase was washed neutral, dried over sodium sulphate, filtered and concentrated in a rotary evaporator. The residue was purified by column chromatography (silica gel; hexane/ethyl acetate = 4:1).

Yield: 12.01 g (29%)
R_f = 0.32 (hexane: ethyl acetate = 8:2)
n_D^{20} = 1.5106

2-(3,4,4-Trifluoro-3-butenyl)malonic acid

5.56 g (99 mmol) KOH flakes were dissolved in 6.82 ml water and 13.65 ml ethanol and then treated with 11.12 g (28.34 mmol) of dibenzyl 2-(3,4,4-trifluoro-3-butenyl)-malonate. After heating under reflux for 4 hours, the reaction mixture was poured into 30 ml water and washed with ether. The aqueous phase was acidified with dilute hydrochloric acid and extracted 4 times with ether. The organic phase was dried over sodium sulphate, filtered and then concentrated in a rotary evaporator.

Yield: 5.95 g (99%)
The product was used without further purification.

Example 17

Process variant b)

3-Phenoxybenzyl 5,6,6-trifluoro-5-hexenoate

A solution of 0.83 ml (5 mmol) Diethyl azodicarboxylate in 10 ml THF was added, dropwise, slowly to a solution of 0.84 g (5 mmol) 5,6,6-trifluoro-5-hexenoic acid, 1.0 g (5 mmol) 3-phenoxybenzyl alcohol and 1.34 g (5 mmol) triphenylphosphine in 15 ml tetrahydrofuran at room temperature. After the mixture had been stirred for 6 hours at room temperature, it was concentrated in a rotary evaporator. The crude product was purified by column chromatography (silica gel; hexane: toluene = 1,1).

Yield: 41%
R_f = 0.19 (hexane/toluene = 1:1)
n_D^{20} = 1.5207

A solution of 4.14 ml (54 mmol) trifluoroacetic acid in 20 ml tetrahydrofuran was added dropwise slowly to a solution of 4-tert-butyldimethylsilyoxybut-1-ylmagnesium chloride [prepared from 36.11 g (162 mmol) 4-chloro-1-tert-butyldimethylsilyloxybutane and 4.21 g (170 mmol) magnesium turnings] in 300 ml tetrahydrofuran. The reaction mixture was heated under reflux for 1 hour, allowed to stand at room temperature overnight and poured into ice-water containing dilute hydrochloric acid. After extraction with ether, the organic phase was washed with ½ saturated aqueous sodium chloride, dried over sodium sulphate, filtered and concentrated. The residue was purified by column chromatography (silica gel; hexane/ethyl acetate = 9:1)

Yield: 12.5 g (47 mmol) 86%

R_f = 0.36 (hexane/ethyl acetate = 8:2)

6, 6-Difluoro-5-trifluoromethyl-1-tert-butyldimethylsilyloxy-5-hexene

A solution of 12.88 g (85.7 mmol) sodium chlorodifluoroacetate in 30 ml diglyme was added dropwise slowly to a solution of 11.50 g (42.9 mmol) 4-trifluoroacetyl-1-tert-butyldimethylsilyloxybutane and 12.54 g (47 mmol) triphenylphosphine in 30 ml diglyme at 165 °C. The mixture was heated for one hour under reflux. After cooling, the crude product was distilled at high vacuum. The distillate which contained diglyme and reaction product was poured into 200 ml water and extracted 4 times, each time with 100 ml ether. The combined ether phases were washed 3 times, each time with 100 ml water, dried over sodium sulphate, filtered and concentrated. The crude product was purified by column chromatography (silica gel; hexane/ethyl acetate = 9:1).

Yield: 6.52 g (48%)

R_f = 0.72 (ethyl acetate)

6,6-Difluoro-5-trifluoromethyl-5-hexenol

A solution of 3.59 g (11.28 mmol) 6,6-difluoro-5-trifluoromethyl-1-tert-butylsilyloxy-5-hexene in 50 ml methanol was treated with a teaspoon full of ion exchange resin and the mixture stirred for 3 hours at room temperature. The ion exchange resin was then filtered off and washed with methanol. The filtrate was carefully concentrated in a rotary evaporator (bath temperature = 35 °C; 200 mbar). The residue was used without further purification.

Example 20

Process variant b)

Hexadecyl 5-bromo-(6,6-difluoro-5-hexenoate)

A solution of 0.8 g (1.5 mmol) hexadecyl 5,6 dibromo-6,6-difluorohexanoate and 0.23 g (1.5 mmol) 1,8-diazabicyclo[5.4.0]undec-7-ene in 50 ml dichloromethane was stirred for 4 hours at room temperature. The reaction mixture was poured into 30 ml water and extracted with dichloromethane. The organic phase was dried over sodium sulphate, filtered and concentrated. The residue was purified by column chromatography (silica gel; hexane/ethyl acetate = 9:1).

Yield: 0.68 g (93%)

$n_D^{23.4}$ = 1.45328

R_f = 0.79 (ethyl acetate)

Preparation of the Starting Material

Hexadecyl 5,6-dibromo-6,6-difluorohexanoate

A solution of 0.54 ml (10.36 mmol) bromine in 10 ml dichloromethane was added dropwise to a solution of 1.94 g (5.18 mmol) hexadecyl 6,6-difluoro-5-hexenoate ester in 15 ml ether at 0 °C. After heating under reflux for 6 hours, the mixture was poured in 100 ml 10% aqueous sodium thiosulphate and extracted with ether. The organic phase was washed with water, dried over sodium sulphate, filtered and concentrated. The residue was purified by column chromatography (silica gel; hexane/ethyl acetate = 9:1).

Yield: 1.65 g (60%)

n_D^{20} = 1.46768

Process variant f)

6,6-Difluoro-5-methyl-5-hexenitrile

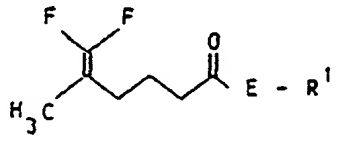
65.9 g Tris(dimethylamino)phosphine was added dropwise to a solution of 42.4 g dibromodifluormethane in 350 ml tetrahydrofuran at 0 to 5 °C. The mixture was heated over 2 hours to 20 °C, cooled to -20 °C, and then treated, dropwise, with a mixture of 15.7 g 5-oxohexanenitrile and 10 ml tetrahydrofuran. The mixture was then stirred at 0 °C for 2 hours and allowed to stand for 12 hours at room temperature. The reaction mixture was poured into 1000 ml water and extracted 3 times with 500 ml n-hexane. After drying the combined organic phases over magnesium sulphate, the solvent was distilled off under slightly reduced pressure and the residue fractionally distilled in vacuo.

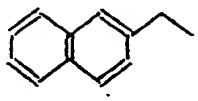
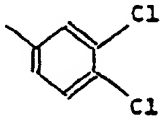
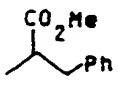
Yield 13.3 g (65%)

bp: 36 °C

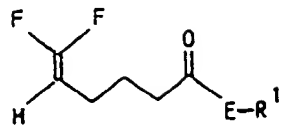
In a similar manner the following compounds were prepared

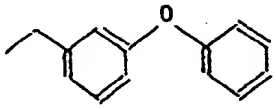
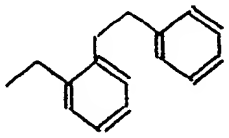
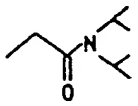
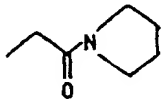
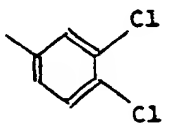
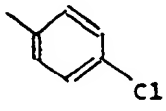
General formula

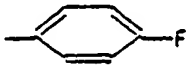
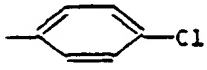
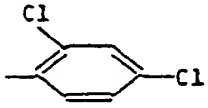
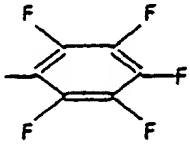
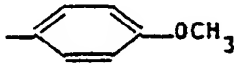
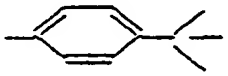


Expl.No.	process	E	R^1	Phys. Const. n_D^{20}	mp (°C)
24	b)	O		1,5429	
25	b)	O	$-C_{16}H_{33}$	1,4386	
26	a)	-NH	H		57-59° C
27	a)	-NH	$-CH_2-C\equiv C-H$		
28	a)	-NH		1,5427	
29	a)	-NH			
30	a)	-NH	$-CH_2-CO_2H$		56-60° C

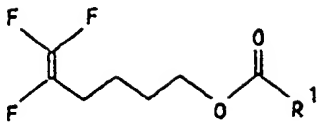
General formula

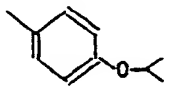
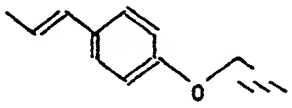


Expl.No.	process	E	R^1	Phys. Const. n_D^{20} or mp (°C)
41	b)	O		1,5269
42	b)	O	$-C_{16}H_{33}$	1,4373
43	b)	O	$-C_{18}H_{37}$	
44	b)	O	$-C_{10}H_{21}$	1,4304
45	b)	O		
46	b)	O		
47	b)	O		1,4662
48	a)	-NH	H	64-67° C
49	a)	-NH	$-CH_2-C\equiv C-H$	1,4524
50	a)	-NH		81-83° C
51	a)	-NH		

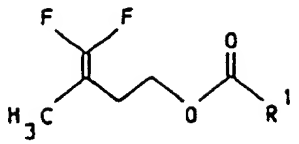
Expl.No.	process	R^1	Phys. Const. n_D^{20} or mp
62	i)		1,4740
63	i)		1,4990
64	i)		1,5128
65	i)		1,4367
66	i)		1,4997
67	h)		1,4895
68	i)	$-C_{17}H_{35}$	1,4620

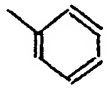
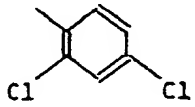
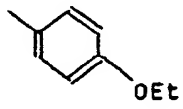
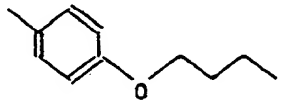
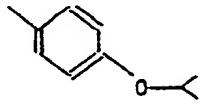
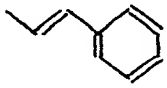
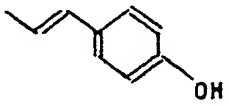
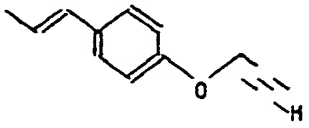
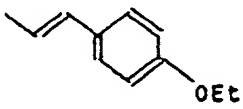
General formula



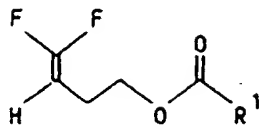
Expl.No.	process	R^1	Phys. Const. n_D^{20} or mp
82	m)	Ph	
83	m)		
84	m)		
85	m)	$-C_{16}H_{33}$	

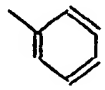
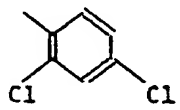
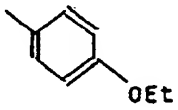
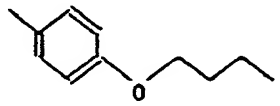
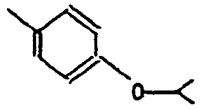
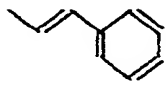
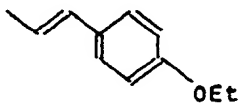
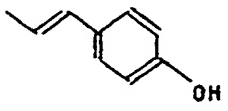
Gen ral formula



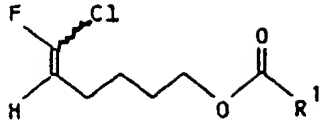
Expl.No.	process	R^1	Phys. Const. n_D^{20} or mp
101	i)		1,4861
102	i)		
103	i)		
104	i)		1,4947 R_F = 0,47 (Hex/EE = 1/1)
105	h)		1,4955
106	h)		
107	h)		
108	h)		1,5542
109	h)		
110	i)	$-C_{16}H_{33}$	

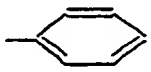
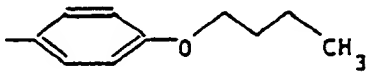
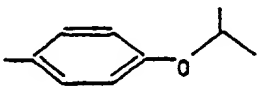
General formula



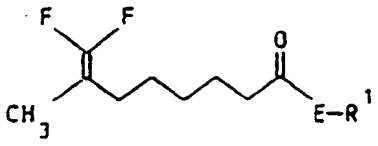
Expl.No.	process	R^1	Phys. Const. n_D^{20} or mp (°C)
124	i)		
125	i)		
126	i)		
127	i)		
128	h)		1,4919
129	h)		
130	h)		
131	h)		
132	i)	$-C_{16}H_{33}$	

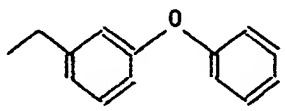
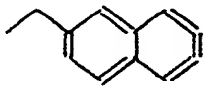
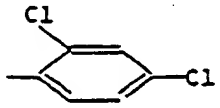
General formula

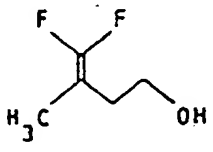
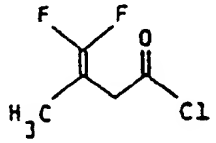
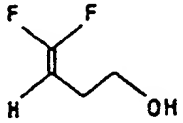
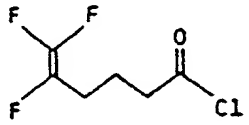
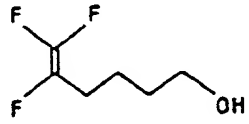
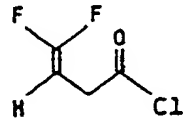
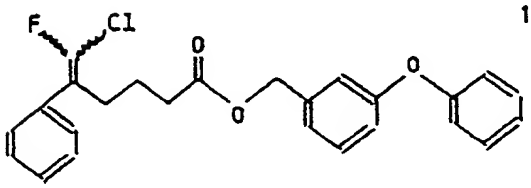
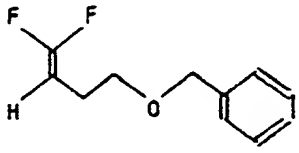


Expl.No.	process	R^1	Phys. Const. n_D^{20} or mp (^oC)
140	i)		1,5073
141	i)		1,5109
142	i)		1,5120

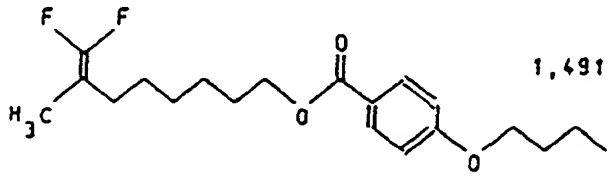
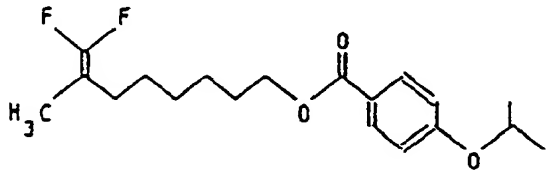
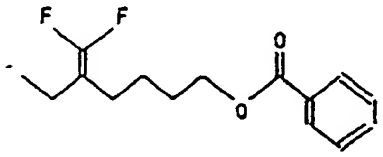
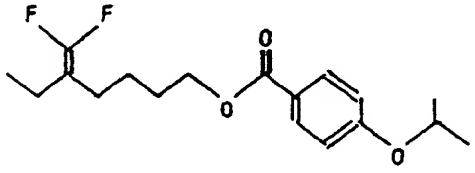
General formula



Expl.No.	process	E	R^1	Phys. Const. n_D^{20} or mp (^oC)
148	c)	O	H	
149	b)	O		1,51962
150	b)	O	$-C_{16}H_{33}$	1,44442
151	b)	O		1,53522
152	a)	-NH		70 ^oC
153	a)	-NH	H	82 ^oC

Expl.No.	process	formula	Physik. Const. n_D^{20} oor mp °C)	R_F
162	j)			0,26*)
163	d)			
164	j)			0,21*)
165	e)			
166	m)			
167	d)			
168	c)		1,5902	
169	j)		1,4701	

*) = Diethyl ther/Hexane = 1/1

Expl.No.	process	formula	Phys. Const. n_D^{20} or mp (°C)
177	i)		1,491
178	h)		1,49156
179	b)		1,48170
180	h)		1,49150

The following test Examples demonstrate the biological activity of the compounds of the invention.

Use Example A

Activity in the prophylactic treatment of feed against the against black bean aphids (Aphis fabae Scop.)

From the primary leaf of field beans (Phaseolus vulgaris nanus Aschers.), 24 mm diameter discs were cut. Some of these were treated with a 0.1% aqueous preparations of compounds of the invention and these along side untreated discs were placed on filter papers with the underside of the leaves turned upwards. After drying the test pieces, they were each infested with wingless stages of Aphis fabae (approx 100 per leaf piece). The experiment was replicated 3 times. The leaves were kept on wet filter papers for 2 days at 25 °C and 16 hours light per day. The percentage mortality was then estimated and the activity calculated using Abbott's method in comparison with the untreated controls.

The compounds of Examples 2, 9, 11-15,20, 30, 38, 41, 42, 44, 47-50, 52, 53, 56-60, 62-64, 66-68, 70, 104, 133-139, 168, 169 and 173 showed an activity of 80% or more.

Use Example B

Activity in prophylactic treatment of leaves against brown rice-hoppers (Nilaparvata lugens Stal)

for four days at 25° C. The % inhibition of hatching of the eggs in comparison with untreated eggs indicates the level of activity.

The compounds of Examples 9, 11-15, 21, 22, 31, 41, 42, 44, 47-50, 52, 53, 55-68, 70, 128, 133-140, 142, 153, 168, 169 and 171 showed 80 - 100% activity.

Use Example G

Activity against larvae (L1) of the cotton bollworm (Heliothis viriscens)

Compounds of the invention were made up as aqueous preparations at a concentration of 0.1%. Into these, feed material was dipped for 2 seconds. After drying the feed material was put into into polystyrene petri dishes. After an hour, 10 L1 of the cotton bollworm (Heliothis viriscens) were counted into the dishes. The closed dishes were left for up to 7 days at 25° C under extended daylight conditions. The % mortality of the larvae after two days indicated the level of activity.

The compounds of Examples 11, 13, 15, 41, 42, 44, 49, 50, 52, 56-58, 70, 128, 133, 134 and 136-139 showed 80 - 100% activity.

Use Example H

Control of root knot nematode (Meloidogyne incognita)

An acetone solution and /or a 5% powder preparation of the active ingredient was mixed thoroughly with soil that had been strongly infested with the test nematode. After this the treated soil was put into a 0.5 litre clay pots. Then cucumber seeds were sown or tomato seedlings planted and cultivated at a soil temperature of 25 to 27° C in a greenhouse. After a cultivation time of 25 to 28 days the cucumber and/or tomato roots were washed and inspected in a water bath for nematode attack (root knots) and the % level of activity of the active ingredients compared with a treated control was determined. When the nematode attack is fully controlled the level of activity is 100%.

At a dose of 10 mg or less of active substance per litre of soil, the compounds of Examples 11, 14, 15, 22, 26, 30, 31, 35, 41, 42, 44, 47-49, 52, 53, 56-58, 60, 62-67, 104, 134-136, 138, 139 and 168 showed 90 - 100% activity.

Use Example I

Insecticidal activity against sheep blowfly (Lucilia sericata)

1 ml aliquots of an acetone solution containing test compound at various concentrations were applied to cotton wool dental rolls 1 cm x 2 cm, contained in glass vials (2 cm diameter x 5 cm long). After drying, the treated materials were then impregnated with 1ml of nutrient solution, infested with first instar larvae of sheep blowfly (Lucilia sericata), closed by a cotton wool plug and held at 25° C for 24 hours.

For the controls the mortality was <5% whereas the compounds of Examples 2, 11, 12-15, 22, 25, 30, 31, 41, 44, 47, 50, 52, 55, 56, 63-65, 68, 74, 101, 105, 138-140, 142, 149, 150 and 152 had an LC_{50} of 300 ppm or less.

Use Example J

Insecticidal activity against house flies (Musca domestica)

Aliquots of acetone solutions of test compounds at various concentrations were applied to 9 cm diameter filter papers placed in the bottom of 9 cm diameter petri dishes closed by glass lids. After evaporation of solvent, the treated surfaces, together with control treated with acetone alone, were then infested with adult houseflies, (Musca domestica) and held at 22° C for 24 hours. The percentage mortality of the insects was then recorded.

Less than 5% mortality resulted in the control treatments whereas the compounds of Examples 13-15, 22, 30, 31, 41, 44, 47, 52, 55, 63-65, 139 and 140 had an LC_{50} of 1000 mg/m^2 or less.

Use Example K

Activity against ticks (Boophilus microplus)

Test compounds were dissolved in a suitable solvent to a desired concentration. Using a microapplicator, 2 microlitres of the solution were injected into the blood filled stomach of a tick (Boophilus microplus). 5 replicate ticks were treated at each concentration and subsequently each tick is retained

cycloalkyl-C_{1-6}-alkyl, halo-C_{3-6}-cycloalkyl-C_{1-6}-alkyl, bicycloalkyl, aryl-C_{1-6}-alkyl, aryl-C_{2-6}-alkenyl, haloaryl-C_{1-6}-alkyl, C_{1-4}-alkylaryl-C_{1-4}-alkyl, haloaryl-C_{2-6}-alkenyl, halo-C_{1-4}-alkylaryl-C_{1-6}-alkyl, C_{1-3}-alkoxyaryl-C_{1-6}-alkyl, aryloxybenzyl, halophenyl(cyclopropyl)-C_{1-3}-alkyl, halophenoxy-C_{1-6}-alkyl, naphthyl-C_{1-6}-alkyl,

aryl, optionally substituted, one or more times, by C_{1-20}-alkyl, halo-C_{1-6}-alkyl, C_{1-16}-alkoxy, halo-C_{1-6}-alkoxy, phenyl-C_{1-6}-alkyl, phenyl-C_{1-6}-alkoxy, C_{3-10}-cycloalkoxy, halo-C_{3-10}-cycloalkoxy, C_{3-6}-cycloalkylalkoxy, halo-C_{3-6}-cycloalkylalkoxy, C_{2-6}-alkenyloxy, halo-C_{2-6}-alkenyloxy, C_{2-6}-alkynyloxy, alkylsulphonyloxy, haloalkylsulphonyloxy, phenyl, halo, amino, cyano, hydroxy, nitro, C_{1-6}-alkoxycarbonyl, C_{1-6}-alkoxycarbonylmethyl, halo-C_{1-6}-alkoxycarbonyl, C_{1-2}-alkyldioxy, C_{1-6}-alkylthio, halo-C_{3-6}-cycloalkylalkylcarbonyloxy, C_{1-6}-alkylamino or di-C_{1-6}-alkylamino,

heteroaryl, optionally substituted by halogen, C_{1-3}-alkyl or halo-C_{1-3}-alkyl, or

R^2 and R^3 together with the N-atom to which they are attached form a saturated or unsaturated heterocyclic ring,

R^4 is hydrogen or -CH(R^5)COOR^8,

R^5 is hydrogen, C_{1-20}-alkyl, C_{2-20}-alkenyl, C_{2-20}-alkynyl, optionally substituted benzyl, aryl or heteroaryl, as well as C_{1-20}-alkyl, C_{2-20}-alkenyl and C_{2-20}-alkynyl, substituted by -Y-R^7, -COOR^7, -NR^{7}R^8, -OCONH$_2$, -NH-C(=NH)-NH$_2$,

R^7 and R^8 are hydrogen or C_{1-6}-alkyl,

Y is oxygen or sulphur, and

R^6 is hydrogen, an alkali metal atom, a corresponding equivalent of a divalent atom or an ammonium or phosphonium cation with 0-4 alkyl, aryl or aralkyl groups, C_{1-20}-alKyl, C_{2-20}-alkenyl, C_{2-20}-alkynyl, halo-C_{3-6}-cycloalkyl-C_{1-6}-alkyl, C_{3-6}-cycloalkyl, C_{1-3}-alkyl-C_{3-6}-cycloalkyl, decalinyl, difluorocyclopropylethylcarbonyloxy-C_{1-10}-alkyl, difluorocyclopropylcarbonyloxydecalinyl,

difluorocyclopropylethylcarbonyloxy-C_{1-3}-alkoxy-C_{1-3}-alkyl, phenyl-C_{1-6}-alkyl, phenyl-C_{2-6}-alkenyl, halobenzyl, C_{1-4}-alkylbenzyl, C_{1-3}-alkoxyphenyl-C_{1-6}-alkyl, phenoxybenzyl, α-cyanophenoxybenzyl, α-C_{1-3}-alkylphenoxybenzyl, halophenoxy-C_{1-6}-alkyl, naphthyl-C_{1-6}-alkyl,

aryl, optionally substituted, one or more times, by C_{1-20}-alkyl, halo-C_{1-6}-alkyl, C_{1-16}-alkoxy, halo-C_{1-6}-alkoxy, phenyl-C_{1-6}-alkyl, phenyl-C_{1-6}-alkoxy, C_{3-10}-cycloalkoxy, halo-C_{3-10}-cycloalkoxy, C_{3-6}-cycloalkylalkoxy, halo-C_{3-6}-cycloalkylalkoxy, C_{2-6}-alkenyloxy, halo-C_{2-6}-alkenyloxy, C_{2-6}-alkynyloxy, halo-C_{2-6}-alkynyloxy, alkylsulphonyloxy, alkylphenylsulphonyloxy, haloalkylsulphonyloxy, phenyl, halo, amino, cyano, hydroxy, nitro, aryloxy, heteroaryloxy, haloaryloxy, arylamino, haloarylamino, C_{1-6}-alkoxycarbonyl, C_{1-6}-alkoxycarbonylmethyl, halo-C_{1-6}-alkoxycarbonyl, C_{1-2}-alkyldioxy, C_{1-6}-alkylthio, halo-C_{3-5}-cycloalkylalkylamino, halo-C_{3-6}-cycloalkylalkylcarbonyloxy, C_{1-6}-alkylamino or di-C_{1-6}-alkylamino,

heteroaryl, optionally substituted by halogen, C_{1-3}-alkyl or halo-C_{1-3}-alkyl,

and

R^4 and R^1 together with the N-atom to which they are attached can form a saturated or unsaturated heterocyclic ring,

with the proviso that when X_1 and X_3 are both fluoro or when X_1 is chloro and X_3 is hydrogen, n is not O, and when X_1 is fluoro and X_3 is trifluoromethyl and n is O, R^1 is not ethyl.

2. An insecticidal and acaricidal composition which comprises a compound as claimed in claim 1 in admixture with an agriculturally acceptable diluent or carrier.

3. Use or a compound according to claim 1, for combating insects or acarids.

4. A method of combating insects and acarids which comprises applying to the insect or acarid or their locus, an effective amount of a compound claimed in claim 1.